Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Impact of the functional group in the polyanion of single lithium-ion conducting polymer electrolytes on the stability of lithium metal electrodes

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Table S1 Characterization data for the ionic conductivities of blended polymer electrolytes of the LiX/PEO (X = PSFSI, PSS, PSTFSI, FSI) with the same molar ratio of EO/Li^+ = 8 and/or 20.

Samples	σ (S cm^{-1})		
(EO/Li^+ ratio by mole)	25 °C	60 °C	90 °C
LiPSFSI/PEO (8)	2.32×10^{-9}	1.43×10^{-5}	5.30×10^{-5}
LiPSFSI/PEO (20)	6.87×10^{-10}	1.11×10^{-6}	3.96×10^{-5}
LiPSS/PEO (20)	2.98×10^{-10}	6.44×10^{-8}	1.92×10^{-7}
LiPSTFSI/PEO (20)	2.09×10^{-9}	1.03×10^{-6}	3.23×10^{-5}
LiFSI/PEO (20)	7.75×10^{-7}	5.29×10^{-4}	2.13×10^{-3}

Table S2 Fitted values for activation energies and correlation coefficients of blended polymer electrolytes of the LiX/PEO (X = PSFSI, PSS, PSTFSI, FSI) with the same molar ratio of EO/Li^+ = 8 and/or 20.

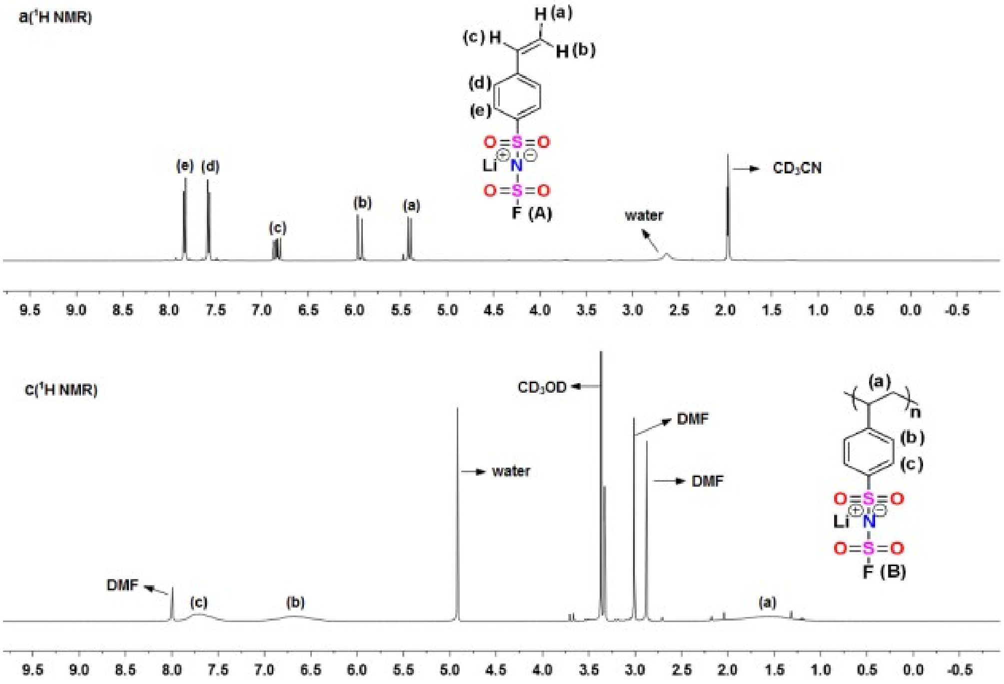
Samples (EO/Li^+ ratio by mole)	Before melting temperature (T_m)		After melting temperature (T_m)	
	Activation energy (E_a) (eV)	Correlation coefficient (R^2) (%)	Activation energy (E_a) (eV)	Correlation coefficient (R^2) (%)
LiPSFSI/PEO (8)	2.18	99.3	0.43	99.6
LiPSFSI/PEO (20)	2.11	99.8	0.53	98.4
LiPSS/PEO (20)	1.94	99.2	0.26	99.0
LiPSTFSI/PEO (20)	1.78	99.7	0.66	98.8
LiFSI/PEO (20)	1.77	99.8	0.46	99.1

$$\sigma = \sigma_0 \exp(-E_a / kT) \quad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

The plots follow an Arrhenius behavior throughout with two regions and with two activation energies. Similar behavior was also observed in other PEO-based polymer electrolytes.[1,2] A comparison of the activation energy values before and after T_m indicates that the conduction process has been changed from crystalline/semi-crystalline phase to amorphous phase.

^{1}H and ^{19}F NMR spectra of the monomer (LiSFSI) and its polymer (LiPSFSI) are shown in Fig. S1. The successful preparation of the polymer salt (LiPSFSI) is well confirmed by comparing the characteristic peaks in ^{1}H and ^{19}F NMR for the monomer (LiSFSI) before and after polymerization reaction. For example, in the ^{1}H NMR spectra, the characteristic peaks for the monomer (LiSFSI) at 5.39−6.87 ppm for the protons of −CH=CH$_2$ group (7.56−7.84 ppm for the phenyl protons) (Fig. S1a) disappeared completely in those of the corresponding products after polymerization (LiPSFSI) (Fig. S1c), and new broad peaks at 1.20−1.90 ppm corresponding to saturated hydrocarbon alkyl are observed, which displays the polymerization occurring at double bonds.[3] Besides, the remarkable differences of ^{19}F NMR spectra between the monomer (a sharp peak) and polymerized products (a broad peak) are also well observed, indicating that the polymer salt (LiPSFSI) is successfully prepared.



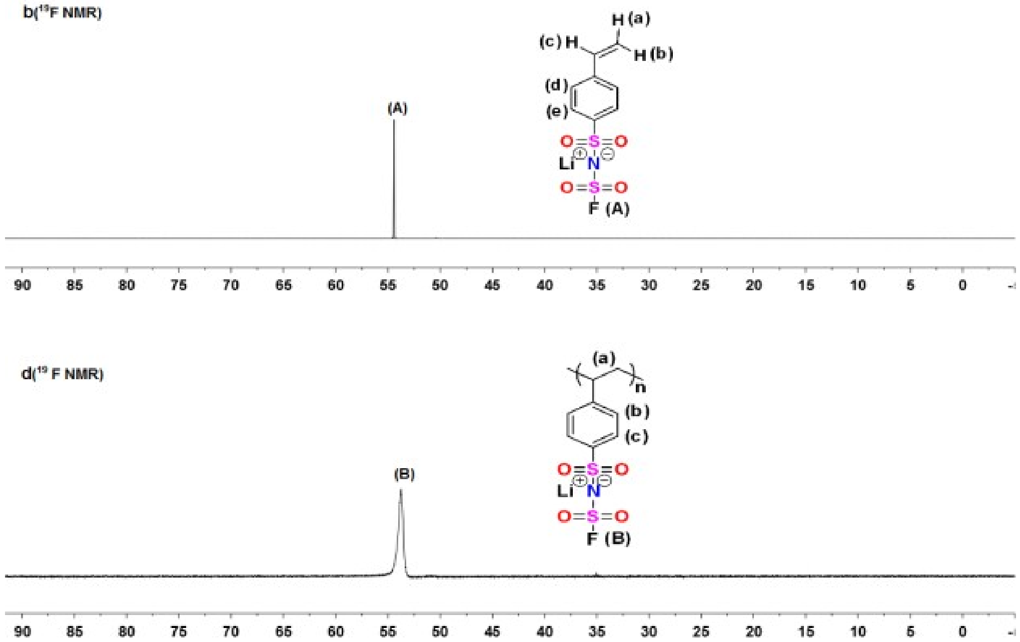


Fig. S1 Comparison of ^{1}H and ^{19}F NMR spectra of the LiSFSI and LiPSFSI.

Fig. S2 shows the TGA traces of the polymer salt (LiPSFSI), and the LiX/PEO (X = PSFSI, PSS) blended polymer electrolytes with the same molar ratio of EO/Li$^+$ = 8 and 20, respectively. As shown in Fig. S2, the neat LiPSFSI salt is thermally stable up to 290 °C without mass loss, which is stable enough for its use as a conducting salt. It is important to note that the decomposition temperatures of the LiPSFSI/PEO blended electrolytes are obviously lower by nearly 150 °C than those of LiPSS/PEO electrolytes, which may be attributed to the less thermal stability of FSO_2– group in the LiPSFSI when compared with the SO_3– group in the LiPSS.[4–6] But they still meet the requirements for application in Li batteries in ambient temperature region.

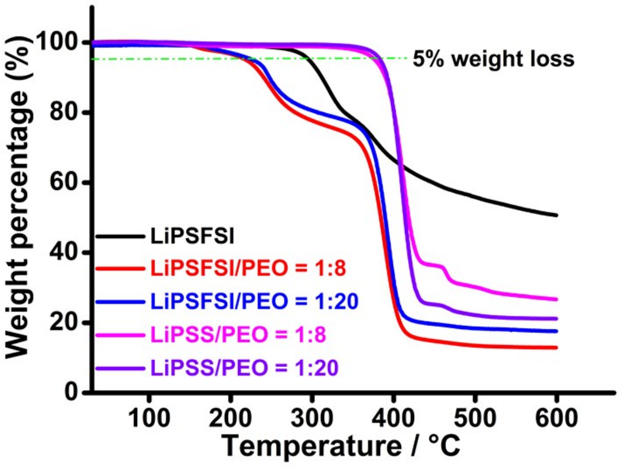


Fig. S2 TGA traces of the polymer salt (LiPSFSI), and the LiX/PEO (X = PSFSI, PSS) blended polymer electrolytes (EO/Li$^+$ = 8 and 20, respectively).

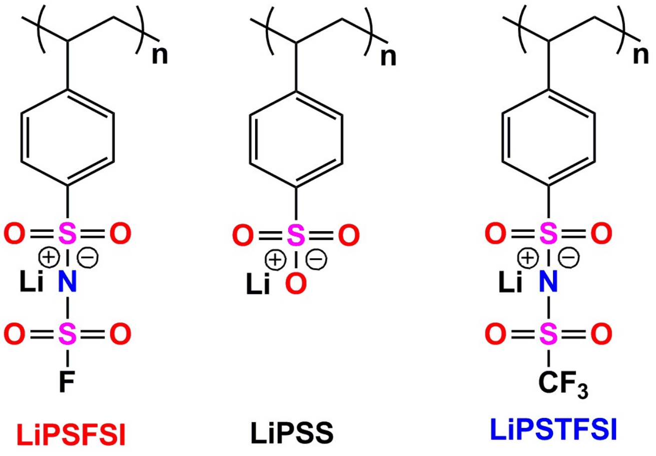


Fig. S3 The representative structures of neat LiX (X = PSFSI, PSS, PSTFSI).

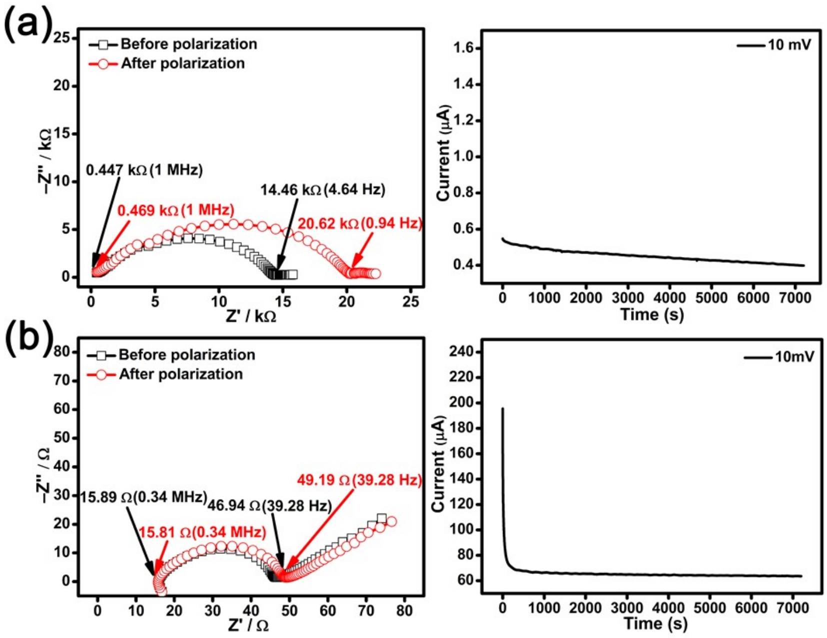


Fig. S4 Impedance spectra and time-dependence response of DC polarization for the complex of LiX/PEO [(a) X = PSFSI (EO/Li^+ = 8), (b) X = FSI (EO/Li^+ = 20)] on the [Li|SPEs|Li] symmetric cells at 70 °C, polarized with a potential of 10 mV.

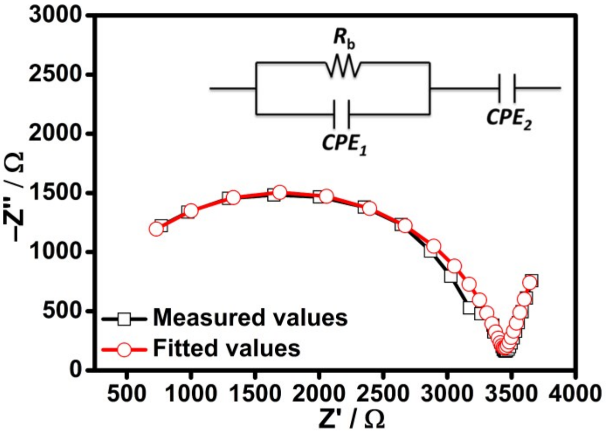


Fig. S5 Measured and fitted EIS spectra for the ionic conductivity of LiPSFSI/PEO (EO/Li$^+$ = 8) blended polymer electrolyte at 70 ^{o}C.

References

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